

Plasma-based chemical modification of epitaxial graphene

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Abstract. In this work, the chemical modification of epitaxial graphene on SiC using electron beam generated plasmas produced in mixtures of argon and oxygen is demonstrated. The treatment imparts oxygen functional groups on the surface with concentrations ranging up to about 12 at.%, depending on treatment parameters. Surface characterization shows the incorporation of oxygen leads to a disruption of π -bonds, and an altering of bulk electrical properties.

Introduction

Graphene, the sp^2 bonded monolayer of carbon atoms, has attracted much attention for its unmatched properties and potential in a wide variety of device applications. Epitaxial graphene (EG), derived from the sublimation of Si from SiC substrates, has been demonstrated to produce a continuous single layer graphene sheet with exceptional properties which holds promise for large scale uniform production [1,2,3] and is of particular interest to the microelectronics industry. However, the use of graphene in devices depends strongly on the ability to manage its properties and on methods to engineer a band gap in this material [4]; chemical doping is one such approach [5,6]. The addition of oxygen, for example, can be used to regulate the conductivity of graphene and can induce the formation of a band gap [7].

There are a number of approaches to incorporating functional groups, either within the plane or on the surface of graphene. Of those, plasma processing represents a well-tested, flexible and scalable technique for materials modification. However, the high energy of ions incident to the substrate surface inherent to many plasma-based tools is of considerable concern in the processing of graphene. Indeed, typical ion energies in high-density, low-pressure systems are above 20 eV and the C-C bond strength is about 3.6 eV, while the low energy thresholds for vacancy creation and displacement in graphite are 7.44 eV [8] and 35 eV [9], respectively.

The Naval Research Laboratory has developed a novel plasma processing tool, which utilizes high-energy electron beams to produce the plasma. When high-energy (~ 2 keV) electron beams are used as the primary ionization source, the resultant plasmas have several unique characteristics when compared to conventional low-pressure plasma sources. Relevant to this work is the inherently low electron temperature, which leads to a low plasma potential and thus limits the energy at which ions impact adjacent surfaces. The electron temperature of the electron beam generated plasmas used in our system varies between about 0.4 and 1 eV [10]. Since the plasma potential is typically 4-5 times the value of the temperature (in volts), the corresponding maximum ion energy at adjacent surface is in the range of 2-5 eV. These values are particularly important in the processing of graphene since they are at or below the aforementioned energy thresholds of

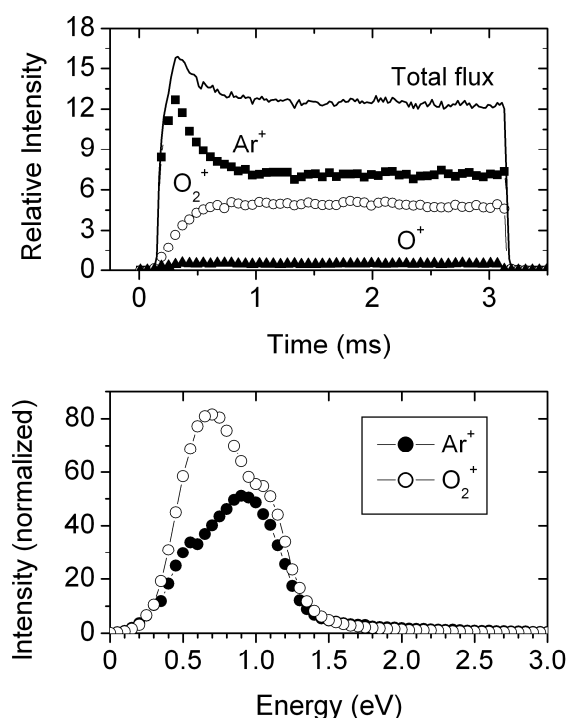


Fig. 1 (Top) Time dependent flux and (Bottom) energy distribution of ions in electron beam generated plasmas produced in Ar/O₂ gas mixtures (50 mTorr).

(II-VI, Inc.) [3] and placed on a grounded substrate holder. Beam pulse widths were 2ms (20 ms period) and the total treatment time was 60 s, resulting in a total plasma exposure time of 6 s. Operating pressures were varied between 50 and 90 mTorr.

A Thermo Scientific K-Alpha X-ray photoelectron spectroscopy (XPS) system equipped with a monochromatic Al-source (1486.6 eV) was used for chemical analysis. Raman characterization was performed using an InVia Raman microscope (Renishaw) equipped with a 50x objective lens, a 514.5nm diode laser excitation on 1800-line grating, at a set source power of 20mW. Hall effect characteristics were measured at room temperature in a van der Pauw configuration, with a magnetic field of 2060 G and measurement currents of 1 and 50 μ A.

Results and Discussion

Shown in Fig 1 are the time-dependent flux of ions and their energy distributions measured at an electrode located adjacent to the plasmas used for the processing of EG. At these pressures and flow rates, Ar⁺ and O₂⁺ ions will comprise the majority of ions, along with a small flux of O⁺ ions. In addition, fluxes of O and photons are expected. This combination of species will provide not only reactive O but also deliver energy to the surface, which facilitates the formation of oxygen functional groups at the surface of graphene. Importantly, the energy of the ions is not high enough to cause any erosion of the grapheme [11]. Generally, an increase in operating pressure will increase the magnitude of the total flux of all species but it will not change the temporal behavior nor the magnitudes of the ion energies [13].

concern, thereby providing a “gentle” modification of the substrate. In previous work [11], we demonstrated the use of these plasmas to decorate the surface of graphene, produced via CVD on copper surfaces, with both fluorine and oxygen. In this work, we report the use of these plasmas to functionalize the surface of epitaxial graphene derived from 6H-SiC.

Experimental

The processing reactor and its operation have been described previously [11]. Briefly, pulsed, sheet-like, 2 keV electron beams were injected into an argon/oxygen background to produce a similarly shaped plasma. Electrodes for diagnostics or processing can be located adjacent to the sheet plasma. For this work, the duty factor was 10% and oxygen was introduced at 5% of the total flow rate.

Ion flux measurements were made using a mass-resolving, ion energy analyzer (Hidden Analytical). Details of the measurement technique can be found in [12].

For plasma functionalization, EG samples were grown by Si sublimation on the Si-face of 8 x 8 mm² semi-insulating 6H-SiC substrates

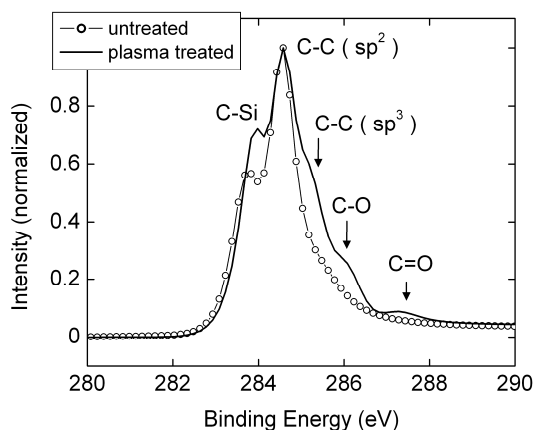


Fig. 2 XPS C1s spectra of untreated (open circles) and plasma treated (solid line) EG. Plasma treatment was performed at 90mT with an Ar/O₂ (5%) plasma.

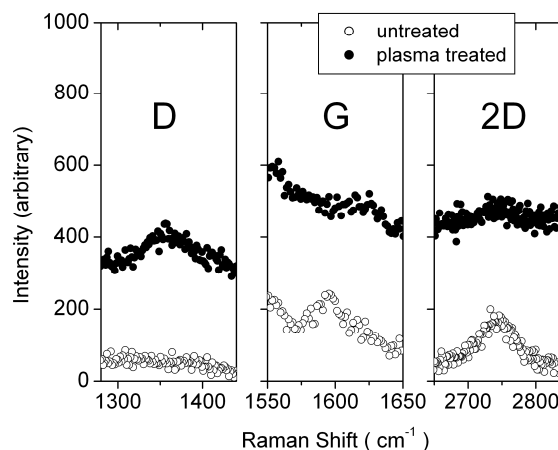


Fig. 3 Snapshots of Raman spectra of EG showing the D, G and 2D modes before (open circles) and after (solid circles) plasma treatment at 90mT.

Chemical and structural changes in EG, due to plasma processing, were tracked using XPS and Raman spectroscopy. As expected, the oxygen content increased with increasing operating pressure, from 3.6 at.% at 50mT to 11.7 at.% at 90 mTorr. A better understanding can be developed by comparing the high-resolution C1s spectra of graphene before and after processing (see Fig. 2). Unprocessed EG was de-convoluted into three components centered at about 283.7eV, 284.5eV and 285.3eV which correspond to (Si-C), (C-C), and the interfacial layer between the SiC and EG, respectively [14]. Following plasma treatment, the C1s spectrum broadened due to the presence of oxygen with peaks corresponding to C-O (286eV) and C=O (287eV). The incorporation of oxygen causes a disruption of sp² hybridization leading to the formation of sp³ hybridization represented by a peak located at about 285.5 eV [11,15].

The details of the binding can be further understood by the Raman spectra, examples of which are shown in Fig. 3. Untreated EG show a weak G peak ($\approx 1600\text{ cm}^{-1}$) and a 2D peak ($\approx 2730\text{ cm}^{-1}$), the latter is indicative of monolayer graphene [16]. The weak intensity of the G peak is attributed to the background contribution of SiC, which was not subtracted; the 2D peak was easily distinguishable from the background. The D to G ratios (I_D/I_G) of the untreated EG samples range from 0.1 to 0.5 demonstrating defect free domains on the order of 200-300nm, as determined from

the equations developed by Tuinstra and Koeing [17,18]. After plasma treatment, the Raman spectra show an increase in the disorder-induced D peak and decreases in the G and 2D peaks.

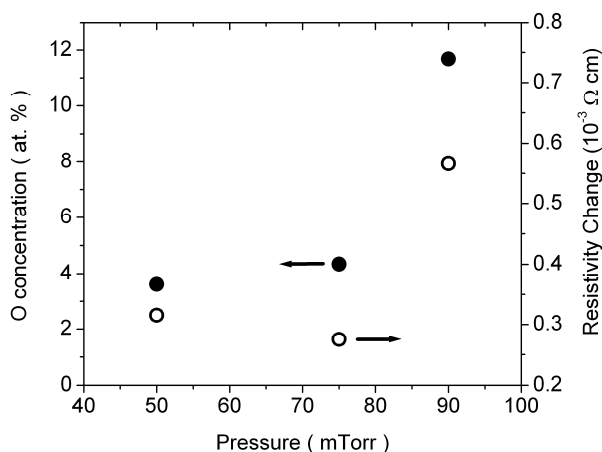


Fig. 4 Dependence of oxygen concentration (solid circles) and change in resistivity (open circles) at different processing pressures.

This addition of oxygen and the subsequent changes in graphene structure increase the resistivity of EG, as can be seen in Fig. 4. Untreated EG samples had an average resistivity of $8.1 \times 10^{-5}\ \Omega\text{ cm}$. EG samples with 3.6-4.3 at.% oxygen correspond to a 5-fold increase in resistivity whereas EG with 11.7at.% oxygen correspond to an 8-fold increase in resistivity. The C-O and C=O entities that are introduced serve as scattering sites for the flow of electrons and so the observed increasing resistivity with increasing oxygen content is to be expected.

Summary

Initial results using electron beam generated plasmas produced in Ar/O₂ to functionalize epitaxial graphene on silicon carbide with oxygen are reported. Plasma diagnostic results show a time-dependent ion flux that is characterized by energies less than 2 eV. Oxygen concentrations on the surface of epitaxial graphene can be increased by increasing the operating pressure. Under all treatment conditions, graphene remained, albeit with increased defects and sheet resistance as a function of increasing oxygen concentrations. It is expected that further control over the oxygen concentrations can be realized by controlling the exposure times.

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